

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problems Mailbox.**

THIS PAGE BLANK (USPTO)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 208 524
A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 86305212.2

(51) Int. Cl. 4: C 08 F 4/64
C 08 F 10/00

(22) Date of filing: 04.07.86

(30) Priority: 05.07.85 JP 146805/85

(43) Date of publication of application:
14.01.87 Bulletin 87/3

(84) Designated Contracting States:
BE DE FR GB IT NL SE

(71) Applicant: TOA NENRYO KOGYO KABUSHIKI KAISHA
1-1 Hitotsubashi, 1-Chome Chiyoda-Ku
Tokyo 100(JP)

(72) Inventor: Furuhashi, Hiroyuki
1902-5, Ooaza Kamekubo Ooi-machi
Iruma-gun Saitama-ken(JP)

(72) Inventor: Yamamoto, Tadashi
1902-5, Ooaza Kamekubo Ooi-machi
Iruma-gun Saitama-ken(JP)

(72) Inventor: Imai, Masafumi
1902-5, Ooaza Kamekubo Ooi-machi
Iruma-gun Saitama-ken(JP)

(72) Inventor: Ueno, Hiroshi
398-1, Ooaza Haneo Namagawa-machi
Hiki-gun Saitama-ken(JP)

(74) Representative: Northover, Robert Frank et al,
ESSO Chemical Limited Esso Chemical Research Centre
P.O. Box 1
Abingdon Oxfordshire, OX13 6BB(GB)

(54) Catalyst component for olefin polymerization.

(57) A titanium containing catalyst component for olefin polymerizations which comprises contacting (a) a metal oxide, (b) a dihydrocarbyl magnesium, and (c) a hydrocarbyloxy group-containing compound with one another, contacting the thus obtained contact product with (d) a halogen-containing alcohol, and finally contacting the thus obtained contact product with (e) an electron donor compound and (f) a titanium compound.

EP 0 208 524 A1

Catalyst Component for Olefin Polymerization 0208524

1 The present invention relates to a reaction product for
2 use in a titanium-containing catalyst component, the
3 titanium-containing catalyst component itself, a catalyst
4 system and an olefin polymerization process.

5

6

7

8

9 Heretofore, there have been proposed several Ziegler-Natta cata-
10 lysts for olefin polymerization in which a metal oxide such as silica
11 and alumina is used as a carrier. Most of them are designed for
12 ethylene polymerization.

13 The proposals include, for example, a catalyst component which is
14 prepared by reacting a porous carrier such as silica with an alkyl
15 magnesium compound, reacting the reaction product with a hydrocarbyl-
16 oxysilane, and further reacting the reaction product with a titanium
17 halide compound (U.S. 4,335,016); and a catalyst component which is
18 prepared by reacting a porous carrier with an organometallic
19 compound, reacting the reaction product with water or a hydrocarbyl
20 alcohol, and further reacting the reaction product with a titanium
21 halide compound (U.S. 4,378,304 and U.S. 4,458,058). Unfortunately,
22 these catalyst components are not suitable for the polymerization of
23 alpha-olefins such as propylene.

24 On the other hand, there are some known catalyst components for
25 the polymerization of propylene. They include, for example, one
26 which is prepared by reacting a metal oxide with a magnesium dial-
27 koxide, and then contacting the reaction product with an electron
28 donor compound and a titanium (IV) halide (Japanese Patent Laid-open
29 No. 162607/1983); one which is prepared by reacting an inorganic
30 oxide with a magnesium hydrocarbyl halide compound, and contacting
31 the reaction product with a Lewis base compound and titanium tetra-
32 chloride (U.S. 4,263,168 and U.S. 4,329,252). These catalyst compo-
33 nents, however, are not satisfactory with regard to activity and
34 stereoregularity.

1 Problems to be solved by the invention

2 It is an object of the present invention to provide a catalyst
3 component supported on a metal oxide which exhibits high activity and
4 high stereoregularity when used for homopolymerization of an olefin,
5 especially alpha-olefin such as propylene, and copolymerization of
6 such an olefin with other olefins.

7 The present inventors previously found a catalyst component
8 which exhibits outstanding catalytic performance in the (co)polymeri-
9 zation of alpha-olefins. (Japanese Patent Publication Number
10 J61021109-A) It is prepared by contacting (a) a metal oxide, (b) a
11 dihydrocarbyl magnesium, and (c) a halogen-containing alcohol with
12 one another, and then contacting the reaction product with (d) an
13 electron donor compound and (e) a titanium compound. In order to
14 improve the performance of the catalyst component, the present invent-
15 tors carried out extensive studies which led to the present invention.

16 Means to solve the problem17 Summary of the invention

18 The gist of the present invention resides in a catalyst compo-
19 nent for olefin polymerization which comprises contacting (A) a metal
20 oxide, (B) a dihydrocarbyl magnesium, and (C) a hydrocarbyloxy group-
21 containing compound with one another, contacting the thus obtained
22 contact product with (D) a halogen-containing alcohol, and finally
23 contacting the thus obtained contact product with (E) an electron
24 donor compound and (F) a titanium compound its process of production,
25 and the precursor comprising the contact product of (A), (B) and (C).

26 Raw materials for preparing the catalyst component27 (A) Metal oxide

28 The metal oxide used in this invention is an oxide of a metal
29 selected from the group of elements in Groups II to IV of the
30 Periodic Table. It includes, for example, B_2O_3 , MgO , Al_2O_3 ,
31 SiO_2 , CaO , TiO_2 , ZnO , ZrO_2 , BaO , and ThO_2 . Preferable among
32 them are B_2O_3 , MgO , Al_2O_3 , SiO_2 , TiO_2 , and ZrO_2 .
33 Especially preferable is SiO_2 . Additional examples of the metal
34 oxides are complex oxides containing these metal oxides, such as
35 SiO_2-MgO , SiO_2-TiO_2 , $SiO_2-V_2O_5$, $SiO_2-Cr_2O_3$, and
36 SiO_2-TiO_2-MgO .

37 Fundamentally, the above-mentioned metal oxides and complex
38 oxides should preferably be anhydrous. However, they may contain a

1 very small amount of hydroxide which is usually present. In addi-
2 tion, they may contain impurities in such an amount that they do not
3 considerably impair the properties of the metal oxides. The permis-
4 sible impurities are oxides, carbonates, sulfates, and nitrates such
5 as sodium oxide, potassium oxide, lithium oxide, sodium carbonate,
6 potassium carbonate, calcium carbonate, magnesium carbonate, sodium
7 sulfate, aluminum sulfate, barium sulfate, potassium nitrate, magne-
8 sium nitrate, and aluminum nitrate.

9 Usually these metal oxides are used in the form of powder. The
10 particle size and shape of the powder should be properly adjusted
11 because they affect the form of the resulting olefin polymer. In
12 addition, the metal oxide should preferably be calcined, prior to
13 use, at as high a temperature as possible to remove poisonous sub-
14 stances, and the calcined metal oxide should be isolated from the
15 atmosphere during handling.

16 (B) Dihydrocarbyl magnesium

17 The dihydrocarbyl magnesium (referred to as organo-Mg herein-
18 after) used in this invention is represented by the formula $RMgR'$,
19 wherein R and R' are the same or different alkyl, cycloalkyl, aryl,
20 and aralkyl groups having 1 to 20 carbon atoms.

21 Examples of the organo-Mg are dimethyl magnesium (magnesium is
22 abbreviated as Mg hereinafter), diethyl Mg, ethylmethyl Mg, dipropyl
23 Mg, diisopropyl Mg, ethyl propyl Mg, dibutyl Mg, diisobutyl Mg,
24 di-sec-butyl Mg, di-tert-butyl Mg, butyl ethyl Mg, butyl propyl Mg,
25 sec-butyl ethyl Mg, tert-butyl isopropyl Mg, sec-butyl tert-butyl Mg,
26 dipentyl Mg, diisopentyl Mg, ethyl pentyl Mg, isopropyl pentyl Mg,
27 sec-butyl pentyl Mg, dihexyl Mg, ethyl hexyl Mg, butyl hexyl Mg,
28 tert-butyl hexyl Mg, (2-ethybutyl) ethyl Mg, (2,2-diethylbutyl) ethyl
29 Mg, diheptyl Mg, dioctyl Mg, di-2-ethylhexyl Mg, di(methylcyclohexyl)
30 Mg, diphenyl Mg, ethyl phenyl Mg, butyl phenyl Mg, sec-butyl phenyl
31 Mg, ditolyl Mg, ethyl tolyl Mg, dixylyl Mg, dibenzyl Mg, benzyl
32 tert-butyl Mg, diphenetyl Mg, and ethyl phenetyl Mg.

33 These organo-Mg compounds may be used in the form of a mixture
34 or complex compound with an organic compound of other metals which is
35 represented by the formula MR_n (where M denotes boron, beryllium,
36 aluminum, or zinc; R denotes an alkyl, cycloalkyl, aryl, or aralkyl
37 group having 1 to 20 carbon atoms; and n denotes the valence of the
38 metal M). Their examples include triethyl aluminum, tributyl alumi-

1 num, triisobutyl aluminum, triphenyl aluminum, triethyl boron, tri-
2 butyl boron, diethyl beryllium, diisobutyl beryllium, diethyl zinc,
3 and dibutyl zinc.

4 Where the organo-Mg is used in the form of a mixture or complex
5 compound with an organic compound of other metals, the amount of
6 other metals is usually less than 5 gram atom, preferably less than 2
7 gram atom, for 1 gram atom of magnesium.

8 (C) Hydrocarbyloxy group-containing compound

9 The hydrocarbyloxy group-containing compound used in this inven-
10 tion is represented by the formula $R''_q M(OR''')_n$ (where R'' denotes
11 a hydrogen atom or a hydrocarbyl group having 1 to 20 carbon atoms; M
12 denotes a silicon, carbon, phosphorous, boron, or aluminum atom; R'''
13 denotes a hydrocarbyl group having 1 to 20 carbon atoms; and $m > q \geq 0$,
14 $M \geq n > 0$, and m denotes the valence of M).

15 Examples of the hydrocarbyl group include alkyl groups such as
16 methyl, ethyl, propyl, i-propyl, butyl, amyl, hexyl, octyl, 2-ethyl-
17 hexyl, and decyl groups, cycloalkyl groups such as cyclopentyl,
18 cyclohexyl, and methylcyclohexyl groups; alkenyl groups such as
19 allyl, propenyl, and butenyl groups; aryl groups such as phenyl,
20 tolyl, and xylyl groups; and aralkyl groups such as phenetyl and
21 3-phenylpropyl groups. Preferably among them are alkyl groups having
22 1 to 10 carbon atoms. R'' and R''' may be the same or different.

23 Examples of these compounds are as follows: Compounds repre-
24 sented by the formula $Si(OR''')_4$ such as $Si(OCH_3)_4$,
25 $Si(C_2H_5)_4$, $Si(OC_4H_9)_4$, $Si(Oi-C_4H_9)_4$, $Si(OC_6H_{13})_4$,
26 $Si(OC_8H_{17})_4$, $Si[O\cdot CH_2CH(C_2H_5)C_4H_9]_4$, and $Si(OC_6H_5)_4$;
27 compounds represented by the formula $R''Si(OR''')_3$ such as
28 $HSi(OC_2H_5)_3$, $HSi(OC_4H_9)_3$, $HSi(OC_6H_{13})_3$, $HSi(OC_6H_5)_3$,
29 $CH_3Si(OCH_3)_3$, $CH_3Si(OC_2H_5)_3$, $CH_3Si(OC_4H_9)_3$,
30 $C_2H_5Si(OC_2H_5)_3$, $C_4H_9Si(OC_2H_5)_3$, $C_6H_5Si(OC_2H_5)_3$, and
31 $C_2H_5Si(OC_6H_5)_3$; compounds represented by the formula $R''_2Si(OR''')_2$
32 such as $(CH_3)_2Si(OCH_3)_2$, $(CH_3)_2Si(OC_2H_5)_2$,
33 $(CH_3)_2Si(OC_3H_7)_2$, $(C_2H_5)_2Si(OC_2H_5)_2$, and
34 $(C_6H_5)_2Si(OC_2H_5)_2$; compounds represented by the formula R''_3SiOR'''
35 such as $(CH_3)_3SiOCH_3$, $(CH_3)_3SiOC_2H_5$, $(CH_3)_3SiOC_4H_9$,
36 $(CH_3)_3SiOC_6H_5$, $(C_2H_5)_3SiOC_2H_5$, and $(C_6H_5)_3SiOC_2H_5$;
37 compounds represented by the formula $C(OR''')_4$ such as $C(OCH_3)_4$,
38 $C(OC_2H_5)_4$, $C(OC_4H_9)_4$, $C(OC_6H_{13})_4$, $C(OC_8H_{17})_4$, and

1 C(OC₆H₅)₄; compounds represented by the formula R''C(OR''')₃ such
2 as HC(OCH₃)₃, HC(OC₂H₅)₃, HC(OC₃H₇)₃, HC(OC₄H₉)₃,
3 HC(OC₆H₁₃)₃, HC(OC₈H₁₇)₃, HC(OC₆H₅)₃, CH₃C(OCH₃)₃,
4 CH₃C(OC₂H₅)₃, and C₂H₅C(OC₂H₅)₃; compounds represented by the
5 formula R''₂C(OR''')₂ such as CH₃CH(OCH₃)₂, CH₃CH(OC₂H₅)₂,
6 CH₂(OCH₃)₂, CH₂(OC₂H₅)₂, and C₆H₅CH(OC₂H₅)₂; compounds
7 represented by the formula P(OR''')₃ such as P(OCH₃)₃, P(OC₂H₅)₃,
8 P(OC₄H₉)₃, P(OC₆H₁₃)₃, and P(OC₆H₅)₃; compounds represented by
9 the formula B(OR''')₃, such as B(OC₂H₅)₃, B(OC₄H₉)₃,
10 B(OC₆H₁₃)₃, and B(OC₆H₅)₃; and compounds represented by the formula
11 Al(OR''')₃, such as Al(OCH₃)₃, Al(OC₂H₅)₃, Al(OCH₃H₇)₃,
12 Al(Oi-C₃H₇)₃, Al(OC₄H₉)₃, Al(Or-C₄H₉)₃, Al(OC₆H₁₃)₃, and
13 Al(OC₆H₅)₃.

14 (D) Halogen-containing alcohol

15 The halogen-containing alcohol used in this invention is a mono-
16 hydric alcohol having one hydroxyl group in one molecule or a poly-
17 hydric alcohol having two or more hydroxyl groups in one molecule,
18 with one or more arbitrary hydrogen atoms other than that of the
19 hydroxyl group replaced by halogen atoms. The halogen atoms are
20 chlorine, bromine, iodine, and fluorine atoms, chlorine atoms being
21 preferable.

22 Examples of the halogen-containing compound include 2-chloro-
23 ethanol, 1-chloro-2-propanol, 3-chloro-1-propanol, 1-chloro-2-
24 methyl-2-propanol, 4-chloro-1-butanol, 5-chloro-1-pentanol,
25 6-chloro-1-hexanol, 3-chloro-1, 2-propanediol, 2-chlorocyclohexanol,
26 4-chlorobenzhydrol, (m,o,p)-chlorobenzyl alcohol, 4-chlorocatechol,
27 4-chloro-(m,o)-cresol, 6-chloro-(m,o)-cresol, 4-chloro-3, 5-dimethyl-
28 phenol, chlorohydroquinone, 2-benzyl-4-chlorophenol, 4-chloro-1-
29 naphthol, (m,o,p)-chlorophenol, p-chloro-alpha-methylbenzyl alcohol,
30 2-chloro-4-phenylphenol, 6-chlorothymol, 4-chlororesorcin, 2-bromo-
31 ethanol, 3-bromo-1-propanol, 1-bromo-2-propanol, 1-bromo-2-butanol,
32 2-bromo-p-cresol, 1-bromo-2-naphthol, 6-bromo-2-naphthol, (m,o,p)-
33 bromophenol, 4-bromoresorcin, (m,o,p)-fluorophenol, p-iodophenol,
34 2,2-dichloroethanol, 2,3-dichloro-1-propanol, 1,3-dichloro-2-
35 propanol, 3-chloro-1-(alpha-chloromethyl)-1-propanol, 2,3-dibromo-1-
36 propanol, 1,3-dibromo-2-propanol, 2,4-dibromophenol, 2,4-dibromo-1-
37 naphthol, 2,2,2-trichloroethanol, 1,1,1-trichloro-2-propanol, B,B,B-
38 trichloro-tert-butanol, 2,3,4-trichlorophenol, 2,4,5-trichlorophenol,

1 2,4,6-trichlorophenol, 2,4,6-tribromophenol, 2,3,5-tribromo-2-
2 hydroxytoluene, 2,3,5-tribromo-4-hydroxytoluene, 2,2,2-trifluoro-
3 ethanol, alpha,alpha,alpha-trifluoro-m-cresol, 2,4,6-triiodophenol,
4 2,3,4,6-tetrachlorophenol, tetrachlorohydroquinone, tetrachlorobis-
5 phenol A, tetrabromobisphenol A, 2,2,3,3-tetrafluoro-1-propanol,
6 2,3,5,6-tetrafluorophenol, and tetrafluororesorcin.

7 (E) Electron donor compound

8 The electron donor compound includes carboxylic acids, carbox-
9 ylic acid anhydrides, carboxylic acid esters, carboxylic acid
10 halides, alcohols, ethers, ketones, amines, amides, nitriles, alde-
11 hydes, alcoholates, phosphamides, thioethers, thioesters, carbonic
12 acid esters, and compounds of phosphorus, arsenic, or antimony
13 attached to an organic group through a carbon or oxygen atom.
14 Preferable among them are carboxylic acids, carboxylic acid anhy-
15 drides, carboxylic acid esters, carboxylic acid halides, alcohols,
16 and ethers.

17 Examples of the carboxylic acids include aliphatic monocar-
18 boxylic acids such as formic acid, acetic acid, propionic acid,
19 butyric acid, isobutyric acid, valeric acid, caproic acid, pivalic
20 acid, acrylic acid, methacrylic acid, and crotonic acid; aliphatic
21 dicarboxylic acids such as malonic acid, succinic acid, glutaric
22 acid, adipic acid, sebacic acid, maleic acid, and fumaric acid; ali-
23 phatic hydroxycarboxylic acids such as tartaric acid; alicyclic car-
24 boxylic acids such as cyclohexane monocarboxylic acid, cyclohexene
25 monocarboxylic acid, cis-1,2-cyclohexane dicarboxylic acid, and cis-
26 4-methylcyclohexene-2,2-dicarboxylic acid; aromatic monocarboxylic
27 acids such as benzoic acid, toluic acid, anisic acid, p-tertiary-
28 butylbenzoic acid, naphthoic acid, and cinnamic acid; and aromatic
29 polycarboxylic acids such as phthalic acid, isophthalic acid, tereph-
30 thalic acid, naphthalic acid, trimellitic acid, hemimellitic acid,
31 trimesic acid, pyromellitic acid, and mellitic acid.

32 The carboxylic acid anhydrides that can be used in this inven-
33 tion are the above-mentioned carboxylic acids in the form of
34 anhydride.

35 The carboxylic acid esters that can be used in this invention
36 are monoesters and polyesters of the above-mentioned carboxylic
37 acids. Their examples include butyl formate, ethyl acetate, butyl
38 acetate, isobutyl isobutyrate, propyl pivalate, isobutyl pivalate,

1 ethyl acrylate, methyl methacrylate, ethyl methacrylate, isobutyl
2 methacrylate, diethyl malonate, diisobutyl malonate, diethyl
3 succinate, dibutyl succinate, diisobutyl succinate, diethyl gluta-
4 rate, dibutyl glutarate, diisobutyl glutarate, diisobutyl adipate,
5 dibutyl sebacate, diisobutyl sebacate, diethyl maleate, dibutyl
6 maleate, diisobutyl maleate, monomethyl fumarate, diethyl fumarate,
7 diisobutyl fumarate, diethyl tartrate, dibutyl tartrate, diisobutyl
8 tartrate, ethyl cyclohexane-carbonate, methyl benzoate, ethyl ben-
9 zoate, methyl p-toluylate, ethyl p-tertiary-butylbenzoate, ethyl
10 p-anisate, ethyl alpha-naphthoate, isobutyl alpha-naphthoate, ethyl
11 cinnamate, monomethyl phthalate, monobutyl phthalate, dibutyl
12 phthalate, diisobutyl phthalate, dihexyl phthalate, dioctyl
13 phthalate, di-2-ethylhexyl phthalate, diaryl phthalate, diphenyl
14 phthalate, diethyl isophthalate, diisobutyl isophthalate, diethyl
15 terephthalate, dibutyl terephthalate, diethyl naphthalate, dibutyl
16 naphthalate, triethyl trimellitate, tributyl trimellitate, tetra-
17 methyl pyrotrimellitate, tetraethyl pyrotrimellitate, and tetrabutyl
18 pyromellitate.

19 The carboxylic acid halides that can be used in this invention
20 are acid halides of the above-mentioned carboxylic acids. Their
21 examples include acetic acid chloride, acetic acid bromide, acetic
22 acid iodide, propionic acid chloride, butyric acid chloride, butyric
23 acid bromide, butyric acid iodide, pivalic acid chloride, pivalic
24 acid bromide, acrylic acid chloride, acrylic acid bromide, acrylic
25 acid iodide, methacrylic acid chloride, methacrylic acid bromide,
26 methacrylic acid iodide, crotonic acid chloride, malonic acid
27 chloride, malonic acid bromide, succinic acid chloride, succinic acid
28 bromide, glutaric acid chloride, glutaric acid bromide, adipic acid
29 chloride, adipic acid bromide, sebatic acid chloride, sebatic acid
30 bromide, maleic acid chloride, maleic acid bromide, fumaric acid
31 chloride, fumaric acid bromide, tartaric acid chloride, tartaric acid
32 bromide, cyclohexane carboxylic acid chloride, cyclohexane carboxylic
33 acid bromide, 1-cyclohexene carboxylic acid chloride, cis-4-methyl-
34 cyclohexene carboxylic acid chloride, cis-4-methylcyclohexene carboxy-
35 lic acid bromide, benzoyl chloride, benzoyl bromide, p-toluic acid
36 chloride, p-toluic acid bromide, p-anisic acid chloride, p-anisic
37 acid bromide, alpha-naphthoic acid chloride, cinnamic acid chloride,
38 cinnamic acid bromide, phthalic acid dichloride, phthalic acid

0208524

1 diacromide, isophthalic acid dichloride, isophthalic acid dibromide,
2 terephthalic acid dichloride, and naphthalic acid dichloride. Additional
3 useful compounds include dicarboxylic acid monoalkylhalides
4 such as adipic acid monomethylchloride, maleic acid monoethyl-
5 chloride, maleic acid monomethylchloride, and phthalic acid butyl-
6 chloride.

7 The alcohols are those compounds represented by the formula ROH,
8 where R is an alkyl, alkenyl, cycloalkyl, aryl, or aralkyl group
9 having 1 to 12 carbon atoms. Examples of the alcohols include metha-
10 nol, ethanol, propanol, isopropanol, butanol, isobutanol, pentanol,
11 hexanol, octanol, 2-thylhexanol, cyclohexanol, benzyl alcohol, allyl
12 alcohol, phenol, cresol, xylenol, ethylphenol, isopropylphenol,
13 p-tert-butylphenol, and n-octylphenol.

14 The ethers are those compounds represented by the formula ROR',
15 where R and R' are alkyl, alkenyl, cycloalkyl, aryl, or aralkyl
16 groups each having 1 to 12 carbon atoms. R and R' may be the same or
17 different. Examples of the ethers include diethyl ether, diisopropyl
18 ether, dibutyl ether, diisobutyl ether, diisoamyl ether, di-2-ethyl-
19 hexyl ether, diallyl ether, ethylallyl ether, butylallyl ether,
20 diphenyl ether, anisole, and ethylphenyl ether. Any one of the
21 above-mentioned halogen-containing alcohols can be used as an
22 electron donor compound.

23 (F) Titanium compound

24 The titanium compound is a compound of divalent, trivalent, or
25 tetravalent titanium. Their examples include titanium tetrachloride,
26 titanium tetrabromide, trichloroethoxytitanium, trichlorobutoxy-
27 titanium, dichlorodiethoxytitanium, dichlorodibutoxytitanium,
28 dichlorodiphenoxytitanium, chlorotriethoxytitanium, chlorotributoxy-
29 titanium, tetrabutoxytitanium, and titanium trichloride. Preferable
30 among them are tetravalent titanium halides such as titanium tetra-
31 chloride, trichloroethoxytitanium, dichlorodibutoxytitanium, and
32 dichlorodiphenoxytitanium. Particularly preferable is titanium
33 tetrachloride.

34 Preparation of catalyst component

35 The preparation of the catalyst component of this invention
36 involves the steps of contacting a metal oxide (component A), an
37 organo-Mg (component B), and a hydrocarbyloxy group-containing
38 compound (component C) with one another, contacting the resulting

1 contact product with a halogen-containing alcohol (component D), and
2 further contacting the resulting contact product with an electron
3 donor compound (component E) and a titanium compound (compound F).

4 Contacting components A, B, and C with one another

5 Components A, B, and C can be contacted with one another in the
6 following four manners.

7 (1) Component A and component B are contacted with each other
8 and the resulting contact product is contacted with component C.

9 (2) Component A and component C are contacted with each other
10 and the resulting contact product is contacted with component B.

11 (3) Component B and component C are contacted with each other
12 and the resulting contact product is contacted with component A.

13 (4) Component A, component B, and component C are contacted with
14 one another simultaneously.

15 The above-mentioned contacting may be accomplished by mixing and
16 stirring or mechanically copulverizing the three components in the
17 presence or absence of an inert medium. Examples of the inert medium
18 include hydrocarbons such as pentane, hexane, heptane, octane,
19 decane, cyclohexane, benzene, toluene, and xylene; and halogenated
20 hydrocarbons such as 1,2-dichloroethane, 1,2-dichloropropane, carbon
21 tetrachloride, butyl chloride, isoamyl chloride, bromobenzene, and
22 chlorotoluene.

23 Usually the contacting of components A, B, and C with one
24 another is performed at -20°C to +150°C for 0.1 to 100 hours. Where
25 the contacting involves heat generation, contacting may be performed
26 in such a manner that the components are mixed little by little at a
27 low temperature in the initial stage, and after the mixing of the
28 entire components is complete, the temperature is increased and
29 contacting is continued. At the interval between contacting steps,
30 the contact product may be washed with one of the above-mentioned
31 inert media; however, in the case of the above-mentioned first and
32 second methods, it is preferable not to wash the contact product of
33 the first two components before it is contacted with the third compo-
34 nent. A preferred molar ratio of components A, B, and C is B/A =
35 0.01 to 10, C/A = 0.01 to 10, and C/B = 0.1 to 10.

36 The contacting of components A, B, and C produces a solid
37 product (referred to as reaction product I hereinafter). If neces-
38 sary, it may be washed with a proper cleaning agent, e.g., one of the

1 above-mentioned inert media, before it undergoes the subsequent
2 contacting steps.

3 Contacting of reaction product I with component D

4 The contacting may be accomplished by mixing and stirring or
5 mechanically copulverizing them in the presence or absence of an
6 inert medium. Contacting should preferably be accomplished by mixing
7 and stirring in the presence of an inert medium. One of the inert
8 media used in the above-mentioned contacting of components A, B, and
9 C may also be used.

10 Usually the contacting of reaction product I with component D
11 (the halogen-containing alcohol) is performed at -20°C to +150°C for
12 0.1 to 100 hours. Where the contacting involves heat generation,
13 contacting may be performed in such a manner that the components are
14 mixed little by little at a low temperature in the initial stage, and
15 after the mixing of all the components is complete, the temperature
16 is increased and contacting is continued. A preferred molar ratio of
17 component D to component B in reaction product I is 0.1 to 20,
18 preferably 0.5 to 10.

19 The contacting of reaction product I with component D produces a
20 solid product (referred to as reaction product II hereinafter). If
21 necessary, it may be washed with a proper cleaning agent, e.g., one
22 of the above-mentioned inert media, before it undergoes the subse-
23 quent contacting steps.

24 Contacting of reaction product II with components E and F

25 Reaction product II is contacted with an electron donor compound
26 (component E) and a titanium compound (compound F) in the following
27 three manners.

28 (1) Reaction product II and component E are contacted with each
29 other and the resulting contact product is contacted with component F.

30 (2) Reaction product II and component F are contacted with each
31 other and the resulting contact product is contacted with component E.

32 (4) Reaction product II, component E, and component F are con-
33 tacted with one another simultaneously.

34 The above-mentioned contacting may be accomplished by mixing and
35 stirring or mechanically copulverizing the three components in the
36 presence or absence of an inert medium. Contacting by mixing and
37 stirring in the presence or absence of an inert medium is prefer-
38 able. Any one of the above-mentioned inert media can be used.

1 Usually the contacting of reaction product II with components E
2 and F is performed at 0°C to 200°C for 0.1 to 100 hours in the case
3 of mechanical copulverization, and 0°C to 200°C for 0.5 to 20 hours
4 in the case of mixing and stirring.

5 The amount of component E is 0.005 to 10 gram mol, preferably
6 0.01 to 1 gram mol, for 1 gram atom of magnesium in reaction product
7 II. The amount of component F is 0.1 gram mol and above, preferably
8 1 to 50 gram mol, for 1 gram atom of magnesium in reaction product II.

9 The contacting of reaction product II with component F may be
10 accomplished more than twice in the same manner as mentioned above.
11 If necessary, the previous contact product may be washed with an
12 inert medium, and component F (and the medium) may be freshly added.

13 In the case where contacting with component F is performed twice
14 or more, the intermediate contact product may be contacted with an
15 inert hydrocarbon, halogenated hydrocarbon, or metal halide compound
16 (component G) prior to the subsequent contact.

17 The inert hydrocarbon that can be used is an aliphatic, alicy-
18 clic, or aromatic hydrocarbons. Their examples are n-hexane, methyl-
19 hexane, dimethylhexane, ethylhexane, ethylmethylpentane, n-heptane,
20 methylheptane, trimethylpentane, dimethylheptane, ethylheptane, tri-
21 methylhexane, trimethylheptane, n-octane, methyloctane, dimethyl-
22 octane, n-undecane, n-dodecane, n-tridecane, n-tetradecane, n-penta-
23 decane, n-hexadecane, n-octadecane, n-nonadecane, n-eicosane, cyclo-
24 pentane, cyclohexane, methylcyclopentane, cycloheptane, dimethyl-
25 cyclopentane, methylcyclohexane, ethylcyclopentane, dimethylcyclo-
26 hexane, ethylcyclohexane, cyclooctane, indan, n-butylcyclohexane,
27 isobutylcyclohexane, adamantane, benzene, toluene, xylene, ethylben-
28 zene, tetramethylbenzene, n-butylbenzene, isobutylbenzene, propyl-
29 toluene, decalin, and tetralin.

30 The halogenated hydrocarbon that can be used is a mono or poly-
31 halogen substituted saturated or unsaturated aliphatic, alicyclic, or
32 aromatic hydrocarbon having 1 to 12 carbon atoms. Their examples
33 derived from aliphatic compounds are methyl chloride, methyl bromide,
34 methyl iodide, methylene chloride, methylene bromide, methylene
35 iodide, chloroform, bromoform, iodoform, carbon tetrachloride, carbon
36 tetrabromide, carbon tetraiodide, ethyl chloride, ethyl bromide,
37 ethyl iodide, 1,2-dichloroethane, 1,2-dibromoethane, 1,2-diido-
38 ethane, methylchloroform, methylbromoform, methyliodoform, 1,1,2-tri-

1 chloroethylene, 1,1,2-tribromoethylene, 1,1,2,2-tetrachloroethylene,
2 pentachloroethane, hexachloroethane, hexabromoethane, n-propyl
3 chloride, 1,2-dichloropropane, hexachloropropylene, octachloro-
4 propane, decabromobutane, and chlorinated paraffin. The examples
5 derived from alicyclic compounds are chlorocyclopropane, tetrachloro-
6 cyclopentane, hexachloropentadiene, and hexachlorocyclohexane. The
7 examples derived from aromatic compounds are chlorobenzene, bromo-
8 benzene, o-dichlorobenzene, p-dichlorobenzene, hexachlorobenzene,
9 hexabromobenzene, benzotrichloride, and o-chlorobenzotrichloride.
10 These compounds may be used individually or in combination with one
11 another.

12 The metal halide compound, or the halide of an element selected
13 from the group of elements in Groups IIIa, IVa, and Va of the
14 Periodic Table (called a metal halide hereinafter) includes the
15 chloride, flouride, bromide, and iodide of B, Al, Ga, In, Tl, Si, Ge,
16 Sn, Pb, As, Sb, and Bi. Preferable among them are BCl_3 , BBr_3 ,
17 BI_3 , AlCl_3 , AlBr_3 , AlI_3 , GaCl_3 , GaBr_3 , InCl_3 , TlCl_3 ,
18 SiCl_4 , SnCl_4 , SbCl_5 , and SbF_5 .

19 Where the contacting with component F is performed twice or more
20 and the intermediate contact product is contacted with an inert
21 hydrocarbon, halogenated hydrocarbon, or metal halide in the interval
22 between the preceding contact and the succeeding contact, the
23 contacting is performed at 0 to 200°C for 5 minutes to 20 hours,
24 preferably at 20 to 150°C for 10 minutes to 5 hours. Where component
25 G is a liquid substance, it should preferably be used in such an
26 amount that contact product II is 1 to 1,000 g per liter of component
27 G. Where component G is a solid substance, it is preferable to use
28 it in the form of solution. It should preferably be used in such an
29 amount that the amount of contact product II is 0.01 to 100 g per g
30 of component G.

31 After the contacting of contact product II with component F, the
32 resulting contact product may be contacted further with component G
33 in the same manner as mentioned above for the contacting with compo-
34 nent G.

35 The catalyst component pertaining to the invention can be
36 produced as mentioned above. The catalyst component thus produced
37 may be washed, if necessary, with an inert hydrocarbon such as

1 hexane, heptane, octane, cyclohexane, benzene, toluene, and xylene,
2 followed by drying, if necessary.

3 The catalyst component of this invention is a powder having a
4 specific surface area of 10 to 1,000 m²/g as measured by the BET
5 method at the adsorption temperature of liquid nitrogen, a pore
6 volume of 0.05 to 5 cm³/g, and a narrow particle size distribution
7 with uniform particle size. It is composed of 3 to 90 wt% of metal
8 oxide, 1 to 25 wt% of magnesium, 0.5 to 10 wt% of titanium, and 4 to
9 60 wt% of chlorine.

10 Catalyst for olefin polymerization

11 The catalyst component obtained in this invention is combined
12 with an organic compound of a metal in Groups I to III of the
13 Periodic Table, to be made into a catalyst for homopolymerization of
14 an olefin or for copolymerization of an olefin with another olefin.

15 Organic compound of metal in Groups I to III

16 An organic compound of lithium, magnesium, calcium, zinc, or
17 aluminum can be used as the organometallic compound. Among these
18 organometallic compounds, an organoaluminum compound is preferable.
19 The organoaluminum compound that can be used is represented by the
20 formula R_m²AlX_{3-m} (where R² is an alkyl group or aryl group;
21 X is a halogen atom, alkoxy group, or hydrogen atom; and m is a
22 number in the range of 1 ≤ n ≤ 3). The examples are alkyl aluminum
23 compounds having 1 to 18 carbon atoms, preferably 2 to 6 carbon
24 atoms, such as trialkyl aluminum, dialkyl aluminum monohalide, mono-
25 alkyl aluminum dihalide, alkyl aluminum sesquihalide, dialkyl alumi-
26 num monoalkoxide, and dialkyl aluminum monohydride, and mixtures
27 thereof and complex compounds thereof. The specific examples include
28 trialkyl aluminum such as trimethyl aluminum, triethyl aluminum,
29 tripropyl aluminum, triisobutyl aluminum, and trihexyl aluminum;
30 dialkyl aluminum monohalide such as dimethyl aluminum chloride,
31 diethyl aluminum chloride, diethyl aluminum bromide, diethyl aluminum
32 iodide, and diisobutyl aluminum chloride; monoalkyl aluminum dihalide
33 such as methyl aluminum dichloride, ethyl aluminum dichloride, methyl
34 aluminum dibromide, ethyl aluminum dibromide, ethyl aluminum
35 diiodide, and isobutyl aluminum dichloride; alkyl aluminum sesqui-
36 halide such as ethyl aluminum sesquichloride; dialkyl aluminum mono-
37 alkoxide such as dimethyl aluminum methoxide, diethyl aluminum
38 ethoxide, diethyl aluminum phenoxide, dipropyl aluminum ethoxide,

1 diisobutyl aluminum ethoxide, and diisobutyl aluminum phenoxide; and
2 dialkyl aluminum hydride such as dimethyl aluminum hydride, diethyl
3 aluminum hydride, dipropyl aluminum hydride, and diisobutyl aluminum
4 hydride.

5 Preferable among these compounds is trialkyl aluminum, particu-
6 larly triethyl aluminum and triisobutyl aluminum. The trialkyl
7 aluminum may be used in combination with other organoaluminum com-
8 pounds such as commercially available diethyl aluminum chloride,
9 ethyl aluminum dichloride, ethyl aluminum sesquichloride, diethyl
10 aluminum ethoxide, and diethyl aluminum hydride, or a mixture thereof
11 or a complex compound thereof.

12 Another organoaluminum compound that can be used is one in which
13 two or more aluminum atoms are connected through an oxygen atom or
14 nitrogen atom. Examples of such compounds are
15 $(C_2H_5)_2AlOAl(C_2H_5)_2$, $(C_4H_9)_2AlOAl(C_4H_9)_2$, and
16 $(C_2H_5)_2AlNAl(C_2H_5)_2$.

17 |

18 C_2H_5

19 Organometallic compounds other than organoaluminum compounds are
20 diethyl magnesium, ethyl magnesium chloride, diethyl zinc,
21 $LiAl(C_2H_5)_4$, and $LiAl(C_7H_{15})_4$.

22 The organometallic compound may be used alone or in combination
23 with an electron donor compound. The electron donor compound may be
24 any compound which is used as component E at the time of preparation
25 of the catalyst component. Other electron donor compounds include
26 organosilicon compounds and those compounds containing a hetero atom
27 such as nitrogen, sulfur, oxygen, and phosphorus.

28 Examples of the organosilicon compounds include tetramethoxy-
29 silane, tetraethoxysilane, tetrabutoxysilane, tetraisobutoxysilane,
30 tetraphenoxy silane, tetra(p-methylphenoxy) silane, tetrabenzyl oxy-
31 silane, methyltriethoxysilane, methyltriethoxysilane, methyltri-
32 butoxysilane, methyltriphenoxysilane, ethyltriethoxysilane, ethyltri-
33 isobutoxysilane, ethyltriphenoxysilane, butyltrimethoxysilane, butyl-
34 triethoxysilane, butyltributoxysilane, butyltriphenoxysilane,
35 isobutyltriisobutoxysilane, vinyltriethoxysilane, aryltrimethoxy-
36 silane, phenyltrimethoxysilane, phenyltriethoxysilane, benzyltri-
37 phenoxy silane, methyltriaryloxy silane, dimethyldimethoxysilane,
38 dimethyldiethoxysilane, dimethyldiisopropoxysilane, dimethyldibutoxy-

1 silane, dimethyldihexyloxysilane, dimethyldiphenoxysilane, diethyl-
2 ethoxysilane, diethylisobutoxysilane, diethyl diphenoxysilane,
3 dibutylisopropoxysilane, dibutyl dibutoxysilane, dibutyl dipheoxy-
4 silane, diisobutyl diethoxysilane, diisobutyl diisobutoxysilane,
5 diphenyl dimethoxysilane, diphenyl diethoxysilane, diphenyl dibutoxy-
6 silane, dibenzyl diethoxysilane, divinyl diphenoxysilane, diaryl dipro-
7 poxysilane, diphenyl diaryloxy silane, methylphenyl dimethoxysilane, and
8 chlorophenyl diethoxysilane.

9 Examples of the electron donor compound containing a hetero atom
10 are given below. Those which contain a nitrogen atom include
11 2,2,6,6-tetramethylpiperidine, 2,6-dimethylpiperidine, 2,6-diethyl-
12 piperidine, 2,6-diisopropylpiperidine, 2,2,5,5-tetramethylpyrro-
13 lidine, 2,5-dimethylpyrrolidine, 2,5-diethylpyrrolidine, 2,5-diiso-
14 propylpyrrolidine, 2-methylpyridine, 3-methylpyridine, 4-methyl-
15 pyridine, 1,2,4-trimethylpiperidine, 2,5-dimethylpiperidine, methyl
16 nicotinate, ethyl nicotinate, nicotinamide, benzoic amide, 2-methyl-
17 pyrrole, 2,5-dimethylpyrrole, imidazole, toluyllic amide, benzoni-
18 trile, acetonitrile, aniline, paratoluidine, orthotoluidine, meta-
19 toluidine, triethylamine, diethylamine, dibutylamine, tetramethylene-
20 diamine, and tributylamine. Those which contain a sulfur atom
21 include thiophenol, thiophene, ethyl 2-thiophenecarboxylate, ethyl
22 3-thiophenecarboxylate, 2-methylthiophene, methylmercaptan, ethyl-
23 mercaptan, isopropylmercaptan, butyl mercaptan, diethyl thioether,
24 diphenyl thioether, methyl benzenesulfonate, methyl sulfite, and
25 ethyl sulfite. Those which contain an oxygen atom include tetra-
26 hydrofuran, 2-methyltetrahydrofuran, 3-methyltetrahydrofuran,
27 2-ethyltetrahydrofuran, dioxane, dimethyl ether, diethyl ether,
28 dibutyl ether, diisoamyl ether, diphenyl ether, anisole, aceto-
29 phenone, acetone, methyl ethyl ketone, acetyl acetone, ethyl
30 2-furoate, isoamyl 2-furoate, methyl 2-furoate, and propyl
31 2-furoate. Those which contain a phosphorus atom include triphenyl
32 phosphine, tributyl phosphine, triphenyl phosphite, tribenzyl phos-
33 phite, diethyl phosphate, and diphenyl phosphate.

34 Two or more kinds of the electron donor compounds may be used.
35 They may be used when the catalyst component is combined with an
36 organometallic compound or used after the contacting with an organo-
37 metallic compound.

1 Usually the organometallic compound is used in an amount of 1 to
2 2000 gram-mol, particularly 20 to 500 gram-mol, per gram-atom of
3 titanium in the catalyst component of this invention.

4 The amount of the organometallic compound is 0.1 to 40 gram-
5 atom, preferably 1 to 25 gram-atom in terms of aluminum per mol of
6 the electron donor compound.

7 Polymerization of olefins

8 The catalyst composed of the catalyst component obtained as
9 mentioned above and an organometallic compound (and an electron donor
10 compound) is useful for homopolymerization of a monoolefin having 2
11 to 10 carbon atoms and also for copolymerization of a monoolefin
12 having 2 to 10 carbon atoms with another monoolefin or a diolefin
13 having 3 to 10 carbon atoms. It is an outstanding catalyst for homo-
14 polymerization of alpha-olefins, particularly alpha-olefins having 3
15 to 6 carbon atoms, such as propylene, 1-butene, 4-methyl-1-pentene,
16 and 1-hexene; and for random and block copolymerization of the above
17 mentioned alpha-olefins with one another and/or with ethylene.

18 The polymerization may be performed in either gas phase or
19 liquid phase. The liquid phase polymerization may be accomplished in
20 an inert hydrocarbon such as n-butane, isobutane, n-pentane, isopen-
21 tane, hexane, heptane, octane, cyclohexane, benzene, toluene, and
22 xylene; or in the liquid monomer. The polymerization temperature is
23 usually -80°C to +150°C, preferably 40°C to 120°C. The polymeri-
24 zation pressure is 1 to 60 atm. The molecular weight modification of
25 the resulting polymer is accomplished by the aid of hydrogen or any
26 known molecular weight modifier present in the system. In the case
27 of copolymerization, the quantity of an olefin to be copolymerized is
28 usually less than 30 wt%, particularly 0.3 to 15 wt%, based on the
29 principal olefin. The polymerization with the catalyst system of
30 this invention may be performed continuously or batchwise under the
31 commonly used conditions. The copolymerization may be accomplished
32 in one step or in two or more steps.

33 Effect of the invention

34 The catalyst component of this invention is effective for the
35 production of polyolefins, particularly isotactic polypropylene,
36 ethylene-propylene random copolymers, and ethylene-propylene block
37 copolymers.

1 The polymerization catalyst containing the catalyst component of
2 this invention has a high polymerization activity and high stereo-
3 regularity and keeps the high activity for a long period at the time
4 of polymerization. In addition, it provides polyolefin powder having
5 a high bulk density and good flowability.

6 Examples

7 The invention is now described in more detail with reference to
8 the following examples and application examples, which are not
9 intended to limit the scope of the invention. Percent (%) in the
10 examples and application examples means wt%, unless otherwise
11 indicated.

12 The heptane insolubles (abbreviated as HI hereinafter) which
13 indicate the ratio of the crystalline phase in the polymer are the
14 amount of the polymer which remains undissolved when the polymer is
15 extracted with boiling n-heptane for 6 hours in a Soxhlet apparatus
16 of improved type.

17 Melt flow rate (MFR) was measured according to ASTM D1238, and
18 bulk density as measured according to ASTM D1896-69, method A.

19 Example 1

20 Contacting of silicon oxide with n-butylethyl magnesium

21 In a 200-ml flask equipped with a dropping funnel and stirrer,
22 with the atmosphere therein replaced with nitrogen, were placed 5 g
23 of silicon oxide (abbreviated as SiO₂ hereinafter) and 40 ml of
24 n-heptane. The silicon oxide is G-952, a product of DAVISON, having
25 a specific surface area of 302 m²/g, a pore volume of 1.54 m³/g,
26 and an average pore diameter of 204 Å. Prior to use, it was calcined
27 in a nitrogen stream at 200°C for 2 hours, and then at 700°C for 5
28 hours). Further, there was added 20 ml of 20% solution of n-butyl-
29 ethylmagnesium (abbreviated as BEM hereinafter) in n-heptane (MAGALA
30 BEM, a product of Texas Alkyls, the solution containing 26.8 mmol of
31 BEM), followed by stirring at 90°C for 1 hour.

32 Contacting with tetraethoxysilane

33 The resulting suspension was cooled to 0°C. To the cooled
34 suspension was added dropwise 20 ml of n-heptane solution containing
35 22.1 g (53.6 mmol) of tetraethoxysilane from the dropping funnel over
36 30 minutes. The reactants were slowly heated to 50°C for 1 hour.
37 After the completion of reaction, the supernatant liquid was removed
38 by decantation. The resulting solid product was washed with 60 ml of

1 n-heptane at room temperature, and the supernatant liquid was removed
2 by decantation. The washing with n-heptane was repeated four times.

3 Contacting with 2,2,2-trichloroethanol

4 The solid product obtained in the above-mentioned step was
5 suspended in 50 ml of n-heptane. To the resulting suspension was
6 added a solution containing 8.0 g (53.6 mmol) of 2,2,2-trichloro-
7 ethanol in 10 ml of n-heptane from a dropping funnel at 0°C over 30
8 minutes. The reactants were slowly heated to 60°C over 1 hour, and
9 stirring was continued at 60°C for 1 hour. After the completion of
10 reaction, the resulting solid product was washed twice with 60 ml of
11 n-heptane and then three times with 60 ml of toluene. The resulting
12 solid product (designated as solid component I) was found to contain
13 36.6% of SiO₂, 5.1% of magnesium, and 38.5% of chlorine. It was
14 also found to have a specific surface area of 257 m²/g and a pore
15 volume of 0.76 cm³/g.

16 Contacting with di-n-butyl phthalate and titanium tetrachloride

17 To the solid component I obtained in the above-mentioned step
18 were added 15 ml of toluene and 0.6 g of di-n-butyl phthalate,
19 followed by reaction at 50°C for 2 hours. Then 40 ml of titanium
20 tetrachloride was added, followed by reaction at 90°C for 2 hours.
21 The resulting solid product was washed eight times with 60 ml of
22 n-hexane at room temperature, followed by drying under reduced pres-
23 sure at room temperature for 1 hour. There was obtained 8.4 g of
24 catalyst component having a specific surface area of 279 m²/g and a
25 pore volume of 0.81 cm³/g. It was also found to contain 53.1% of
26 SiO₂, 7.4% of magnesium, 24.8% of chlorine, and 3.1% of titanium.

27 Example 2

28 The solid product obtained after the contacting with titanium
29 tetrachloride in Example 1 was separated, and it was reacted with 40
30 ml of titanium tetrachloride at 90°C for 2 hours. The resulting
31 solid product was treated in the same manner as in Example 1. Thus
32 there was obtained a catalyst component containing 3.2% of titanium.

33 Example 3

34 After the contacting with titanium tetrachloride in Example 1,
35 the supernatant liquid was removed by decantation, and the solid
36 produce was washed with 60 ml of toluene at 90°C for 15 minutes.
37 Washing with toluene was repeated. To the solid product were added
38 15 ml of toluene and 40 ml of titanium tetrachloride, followed by

1 reaction at 90°C for 2 hours. After washing with n-hexane and drying
2 in the same manner as in Example 1, there was obtained a catalyst
3 component containing 3.1% of titanium.

4 Example 4

5 A catalyst component (83 g) was prepared in the same manner as
6 in Example 3, except that the contacting with titanium tetrachloride
7 was performed at 120°C instead of 90°C. The catalyst component was
8 found to have a specific surface area of 283 m²/g and a pore volume
9 of 0.79 cm³/g. It was also found to contain 53.5% of SiO₂, 7.3%
10 of magnesium, 24.5% of chlorine, and 2.6% of titanium.

11 Example 5

12 A catalyst component containing 2.5% of titanium was prepared in
13 the same manner as in Example 4, except that di-n-butyl phthalate and
14 titanium tetrachloride were added simultaneously to solid component I
15 instead of separately.

16 Example 6

17 A catalyst component containing 2.4% of titanium was prepared in
18 the same manner as in Example 4, except that the contacting of solid
19 component I with di-n-butyl phthalate and titanium tetrachloride was
20 performed as follows: At first, 60 ml of titanium tetrachloride was
21 added, followed by rapid heating to 120°C, and then 0.6 g of di-n-
22 butyl phthalate was added, followed by reaction at 120°C for 2 hours.

23 Example 7

24 To solid component I obtained in Example 1 was added 60 ml of
25 titanium tetrachloride, followed by rapid heating to 120°C with
26 stirring; and then 0.6 g of di-n-butyl phthalate was added, followed
27 by reaction at 90°C for 2 hours. After the completion of reaction,
28 the supernatant liquid was removed and 60 ml of titanium tetra-
29 chloride was added, followed by reaction at 120°C for 2 hours. The
30 resulting solid product was washed and dried in the same manner as in
31 Example 1. Thus there was obtained a catalyst component containing
32 2.9% of titanium.

33 Example 8

34 A catalyst component containing 3.9% of titanium was prepared in
35 the same manner as in Example 7, except that the solid component I
36 was washed twice with 60 ml of titanium tetrachloride at 90°C for 15
37 minutes at the interval between the first and second contacting with
38 titanium tetrachloride.

1 Examples 9 to 11

2 Example 4 was repeated, except that toluene as the inert medium
3 used in the contacting with di-n-butyl phthalate and titanium tetra-
4 chloride was replaced by xylene (Example 9), n-heptane (Example 10),
5 or 1,2-dichloroethane (Example 11). The titanium content in each
6 catalyst component was 2.7% (Example 9), 2.9% (Example 10), and 2.5%
7 (Example 11).

8 Examples 12 to 15

9 Example 4 was repeated, except that SiO_2 was replaced by the
10 metal oxide shown below. Thus there were obtained catalyst compo-
11 nents each containing titanium as shown below.

Example	Metal oxide	Conditions of calcination	Titanium content (%)
12	Al_2O_3	200°C/2 hours 700°C/5 hours	3.3
13	$(\text{MgO})_2(\text{SiO}_2)_3$	200°C/2 hours 500°C/5 hours	3.0
14	Mixture of 1 kg of SiO_2 and 100 g of Al_2O_3	200°C/2 hours 700°C/5 hours	2.9
15	Mixture of 1 kg of SiO_2 and 20 g of CrO_3	200°C/2 hours 700°C/5 hours	2.5

12 Examples 16 to 18

13 Example 4 was repeated, except that the BEM was replaced by the
14 organo-Mg shown below. Thus there were obtained catalyst components
15 each containing titanium as shown below.

Example	Organic Mg	Titanium content (%)
16	Di-n-hexylmagnesium (MAGALA DNHM, made by Texas Alkyls)	2.5
17	Di-n-butylmagnesium (0.5 mol) - triethyl aluminum (1 mol) complex, (MAGALA 0.5E, made by Texas Alkyls)	2.6
18	Di-n-butylmagnesium (7.5 mol) - triethyl aluminum (1 mol) complex, (MAGALA 7.5E, made by Texas Alkyls)	2.5

1 Examples 19 to 26

2 Example 4 was repeated, except that tetraethoxysilane was
3 replaced by the hydrocarbyloxy group-containing organic compound
4 shown below. Thus there were obtained catalyst components each
5 containing titanium as shown below.

Example	Hydrocarbyloxy group containing compound*	Titanium content (%)
19	Si(On-Bu) ₄	2.5
20	Si(OPh) ₄	2.9
21	PhSi(OEt) ₃	2.6
22	C(OEt) ₄	2.4
23	HC(OEt) ₃	2.6
24	P(OEt) ₃	3.0
25	B(OEt) ₃	3.1
26	Al(OEt) ₃	2.9

* Bu=C₄H₉, Ph=C₆H₅, Et=C₂H₅

6 Examples 27 to 45

7 Example 4 was repeated, except that 2,2,2-trichloroethanol was
8 replaced by the halogen-containing alcohol shown below. Thus there

1 were obtained catalyst components each containing titanium as shown
2 below.

Example	Halogen-containing alcohol	Titanium content (%)
27	1,1,1-trichloro-2-propanol	2.4
28	B,B,B-trichloro-tert-butanol	2.6
29	2,2-dichloroethanol	2.8
30	1,3-dichloro-2-propanol	2.7
31	2-chloroethanol	2.9
32	4-chloro-1-butanol	2.9
33	6-chloro-1-hexanol	2.8
34	p-chlorophenol	3.0
35	4-chloro-o-cresol	3.1
36	2,4,6-trichlorophenol	2.5
37	tetrachlorohydroquinone	2.6
38	1-bromo-2-butanol	2.7
39	1,3-dibromo-2-propanol	2.8
40	p-bromophenol	2.9
41	2,4,6-tribromophenol	2.8
42	p-iodophenol	2.7
43	2,4,6-triiodophenol	3.0
44	2,2,2-trifluoroethanol	2.8
45	p-fluorophenol	2.8

3 Examples 46 to 70

4 Example 4 was repeated, except that the solid component I was
5 contacted with an electron donor compound shown below in place of
6 di-n-butyl phthalate. Thus there were obtained catalyst components
7 each containing titanium as shown below.

Example	Electron donor compound	Titanium content (%)
46	Ethyl benzoate	2.2
47	Diisobutyl phthalate	2.7
48	Phthalic anhydride	2.3
49	Phthalic dichloride	2.5
50	n-Butyl phthalate chloride	2.4
51	Mono-n-butyl phthalate	2.4
52	Benzoic anhydride	2.9
53	Benzoyl chloride	2.0
54	Ethyl cinnamate	2.9
55	Ethyl cyclohexanecarboxylate	2.8
56	Tartaric acid	2.6
57	Di-n-butyl tartrate	2.3
58	Isobutyl methacrylate	2.5
59	Phthalic acid	2.4
60	Benzoic acid	3.0
61	Di-n-butyl maleate	3.1
62	Diisobutyl sebacate	2.7
63	Tri-n-butyl trimellitate	2.6
64	Ethanol	2.9
65	Isobutanol	2.7
66	2-Ethylhexanol	2.6
67	p-Cresol	2.8
68	Diethyl ether	2.0
69	Di-n-butyl ether	2.1
70	Diphenyl ether	2.1

0208524

1 Example 71

2 Contacting of silicon oxide with tetraethoxysilane

3 In a 200-ml flask equipped with a dropping funnel and stirrer,
4 with the atmosphere therein replaced with nitrogen, were placed 5 g
5 of silicon oxide (the one used in Example 1) and 40 ml of n-heptane
6 and 11.2 g of tetraethoxysilane. Contacting was performed by stir-
7 ring at 90°C for 1 hour.

8 Contacting with n-butylethyl magnesium

9 The suspension obtained in the above step was cooled to 0°C. To
10 the cooled suspension was added a solution containing 20 ml of BEM in
11 20 ml of n-heptane from the dropping funnel over 30 minutes. Stir-
12 ring was continued at 50°C for 1 hour. After the completion of
13 reaction, the resulting solid product was washed five times with 60
14 ml of n-heptane by decantation.

15 Contacting with 2,2,2-trichloroethanol, di-n-butyl phthalate, and
16 titanium tetrachloride

17 The solid component obtained in the above-mentioned step was
18 contacted with 2,2,2-trichloroethanol, di-n-butyl phthalate, and
19 titanium tetrachloride in the same manner as in Example 4. Thus
20 there was obtained 8.5 g of catalyst component containing 2.6% of
21 titanium.

22 Example 72

23 Contacting of n-butylethyl magnesium with tetraethoxysilane

24 In a 200-ml flask equipped with a dropping funnel and stirrer,
25 with the atmosphere therein replaced with nitrogen, were placed 20 ml
26 of BEM solution (the one used in Example 1) and 40 ml of n-heptane,
27 followed by cooling to 0°C. To the cooled reactants was added a
28 solution containing 11.2 g of tetraethoxysilane in 20 ml of n-heptane
29 from the dropping funnel over 30 minutes to give a uniform solution.

30 Contacting with silicon oxide

31 In a 200-ml flask equipped with a dropping funnel and stirrer,
32 with the atmosphere therein replaced with nitrogen, were placed 5 g
33 of SiO₂ (the one used in Example 1) and 20 ml of heptane, following
34 by cooling to 0°C. While the temperature was kept at 0°C, the
35 above-mentioned solution was added. The reactants were slowly heated
36 to 50°C over 1 hour, and stirring was continued at 59°C for 1 hour.
37 After the completion of reaction, the solid product was washed five
38 times with 60 ml of n-heptane by decantation.

1 Contacting with 2,2,2-trichloroethanol, di-n-butyl phthalate, and
2 titanium tetrachloride

3 The solid component obtained in the above-mentioned step was
4 contacted with 2,2,2-trichloroethanol, di-n-butyl phthalate, and
5 titanium tetrachloride in the same manner as in Example 4. Thus
6 there was obtained 8.8 g of catalyst component containing 2.5% of
7 titanium.

8 Comparative Example 1

9 Example 4 was repeated, except that treatment with 2,2,2-tri-
10 chloroethanol was not performed. There was obtained 8.7 g of cata-
11 lyst component containing 3.5% of titanium.

12 Comparative Example 2

13 Example 4 was repeated, except that treatment with tetraethoxy-
14 silane was not performed and washing with n-heptane was performed
15 before treatment with 2,2,2-trichloroethanol. There was obtained 7.0
16 g of catalyst component containing 2.1% of titanium.

17 Application Example 1

18 Into a 1.5-liter stainless steel autoclave equipped with a
19 stirrer was charged under a nitrogen atmosphere a mixture prepared by
20 mixing the following constituents, followed by standing for 5
21 minutes. (a) 30.3 mg of the catalyst component obtained in Example
22 1. (b) 0.97 ml of solution containing 1 mol of triethylaluminum
23 (abbreviated as TEAL hereinafter) in 1 liter of n-heptane. (c) 0.97
24 ml of solution containing 0.1 mol of phenyltriethoxysilane (abbre-
25 viated as PES hereinafter) in 1 liter of n-heptane. Then 0.1 liters
26 of hydrogen gas as a molecular weight modifier and 1 liter of liqui-
27 fied propylene were forced into the autoclave. The reaction system
28 was heated to 70°C and the polymerization of propylene was carried
29 out for 1 hour. After the completion of polymerization, unreacted
30 propylene was purged. There was obtained 206 g of white polypro-
31 pylene powder having an HI of 97.0%, an MFR of 4.9, and a bulk
32 density of 0.42 g/cm³. [Kc (amount of polymer (g) produced per
33 gram of the catalyst component) = 6,800, and Kt (amount of polymer
34 (kg) produced per gram of titanium in the catalyst component) = 219].

35 Application Examples 2 to 74

36 Polymerization of propylene was carried out in the same manner
37 as in Application Example 1, except that the catalyst components

0208523

1 obtained in Examples 2 to 12 and Comparative Examples 1 and 2 were
2 used. The results are shown in the following table.

Application Example	Catalyst Component	Kc (g/g·cat)	Kt (kg/g·Ti)	HI (%)	MFR (g/10 min)	Bulk Density (g/cm ³)
2	Example 2	6900	216	97.1	5.6	0.42
3	Example 3	7400	299	97.5	6.2	0.43
4	Example 4	8100	312	97.9	4.9	0.43
5	Example 5	7900	316	97.8	7.7	0.43
6	Example 6	7600	317	97.8	6.8	0.43
7	Example 7	7200	248	97.4	5.1	0.42
8	Example 8	7500	250	97.6	4.3	0.42
9	Example 9	7300	270	97.7	6.9	0.42
10	Example 10	6900	238	97.4	5.5	0.42
11	Example 11	7900	316	97.9	7.3	0.43
12	Example 12	7300	221	96.9	4.1	0.41
13	Example 13	6700	223	96.5	7.1	0.39
14	Example 14	5800	234	95.9	8.6	0.39
15	Example 15	6200	248	96.1	6.3	0.40
16	Example 16	7700	308	97.8	4.6	0.43
17	Example 17	7600	292	97.8	7.5	0.43
18	Example 18	7300	292	97.6	6.6	0.42
19	Example 19	7900	316	98.0	7.9	0.43
20	Example 20	6400	221	97.0	5.3	0.42
21	Example 21	7700	296	97.7	4.6	0.42
22	Example 22	6900	288	97.1	8.1	0.42
23	Example 23	6800	283	96.9	5.5	0.42
24	Example 24	5900	197	95.5	4.8	0.41
25	Example 25	6100	197	95.9	6.7	0.41
26	Example 26	6500	224	96.1	3.9	0.41
27	Example 27	7300	306	97.7	4.5	0.43
28	Example 28	7700	297	97.8	5.1	0.43
29	Example 29	6500	232	97.5	5.8	0.42
30	Example 30	6600	244	97.3	5.5	0.42

0208524

31	Example 31	6300	217	97.3	6.3	0.42
32	Example 32	6300	217	97.2	5.8	0.42
33	Example 33	6000	214	97.2	6.9	0.41
34	Example 34	7200	240	97.5	5.1	0.43
35	Example 35	6900	223	97.6	4.6	0.43
36	Example 36	7300	292	97.5	6.4	0.43
37	Example 37	5900	227	97.2	6.7	0.41
38	Example 38	5600	207	97.1	7.5	0.41
39	Example 39	6100	218	96.8	5.6	0.41
40	Example 40	6400	221	96.7	6.8	0.41
41	Example 41	5700	204	97.1	5.7	0.42
42	Example 42	5500	204	96.5	4.3	0.41
43	Example 43	6000	200	97.1	7.9	0.42
44	Example 44	6800	243	97.0	4.9	0.43
45	Example 45	6700	239	97.1	6.3	0.43
46	Example 46	6600	300	95.4	5.0	0.43
47	Example 47	7900	293	97.9	4.2	0.43
48	Example 48	7100	309	97.5	4.6	0.42
49	Example 49	7600	304	97.8	5.3	0.43
50	Example 50	6900	288	97.2	3.9	0.43
51	Example 51	6800	283	97.4	6.7	0.42
52	Example 52	5900	203	96.1	4.4	0.42
53	Example 53	6500	325	95.8	4.9	0.42
54	Example 54	5400	186	96.3	7.3	0.41
55	Example 55	5800	207	96.5	6.7	0.41
56	Example 56	5300	204	95.9	5.5	0.41
57	Example 57	6200	270	96.1	5.8	0.42
58	Example 58	6600	254	96.6	7.4	0.42
59	Example 59	6800	283	97.1	4.9	0.42
60	Example 60	6300	210	95.8	3.8	0.41
61	Example 61	7000	226	96.5	5.9	0.42
62	Example 62	6900	256	97.1	4.3	0.42
63	Example 63	7300	281	97.5	5.4	0.43
64	Example 64	5400	186	95.2	7.3	0.41
65	Example 65	5700	211	95.4	5.2	0.41
66	Example 66	6000	236	95.5	4.8	0.42
67	Example 67	6100	218	96.1	6.4	0.42
68	Example 68	4900	245	95.3	7.9	0.40

69	Example 69	5600	267	95.8	8.6	0.41
70	Example 70	5900	281	96.0	6.3	0.41
71	Example 71	8000	308	97.9	4.8	0.43
72	Example 72	7800	312	97.8	5.3	0.43
73	Compar.	3700	106	95.7	8.9	0.41
	Example 1					
74	Compar.	3900	186	98.0	5.1	0.43
	Example 2					

1 The polypropylene powder obtained in Application Example 4 was
2 examined for particle size distribution. The results are shown below.

	Particle diameter (μm)	Distribution
4	Smaller than 149	0
5	149 to 250	0.1
6	250 to 350	2.1
7	350 to 420	5.7
8	420 to 590	24.8
9	590 to 840	41.4
10	840 to 1000	12.1
11	1000 to 1680	13.7
12	Larger than 1680	0.1

13 Application Example 75

14 Gas-phase polymerization of propylene

15 In a 5-liter autoclave equipped with a stirrer was placed 150 g
16 of polypropylene powder which had previously been dried at 90°C for 4
17 hours in a nitrogen stream. To this autoclave, with the stirrer run-
18 ning at 150 rpm, were fed the catalyst component prepared in the same
19 manner as in Example 4 (at a rate of 20 mg/hour), TEAL (at a rate of
20 0.7 mmol/hour), PES (at a rate of 0.05 mmol/hour), propylene (at a
21 rate of 130 g/hour), and hydrogen gas (at a rate of 15 ml/hour).
22 Polymerization of propylene was performed continuously at a polymeri-
23 zation temperature of 70°C and under a polymerization pressure of 20
24 kg/cm², and the polymerization product was discharged continu-

ously. There was obtained polypropylene powder at a rate of 85 g/hour. The polymer had an MFR of 5.9 g/10 min and an HI of 96.9%.

Application Example 76

Block copolymerization of propylene

Into a 1.5 liter autoclave equipped with a stirrer was charged under a nitrogen atmosphere a mixture prepared by mixing the following constituents, followed by standing for 5 minutes. (a) 30.0 mg of the catalyst component obtained in Example 4. (b) 0.75 ml of TEAL solution (1 mol/liter) in n-heptane. (c) 0.75 ml of PES solution (0.1 mol/liter) in n-heptane. Then 100 ml of hydrogen gas and 1 liter of liquified propylene were forced into the autoclave. The reaction system was heated to 70°C and the homopolymerization of propylene was carried out for 1 hour. (According to the polymerization experiment carried out separately under the same condition, the resulting polypropylene had an HI of 97.9%.) After the completion of polymerization, unreacted propylene was purged and the atmosphere in the autoclave was replaced with nitrogen gas. Then an ethylene-propylene mixture gas [ethylene/propylene = 1.5 (molar ratio)] was introduced continuously so that the monomer gas pressure was kept at 1.5 atm. Copolymerization was carried out at 70°C for 3 hours. After the completion of polymerization, unreacted mixture gas was purged. Thus there was obtained 219 g of propylene block copolymer.

The ratio of the copolymer portion was calculated at 25.8% on the basis of the consumption of mixture gas and the total amount of polymer produced. The content of ethylene in the entire polymer was 12.6% according to infrared spectrophotometry. This translates into an ethylene content of 49% in the copolymer fraction. The amounts of propylene homopolymer and copolymer fractions produced per g of catalyst component were 7900 g and 275 g, respectively, which were calculated from the total amount of polymer produced and the consumption of mixture gas. The resulting block copolymer had an MFR of 2.7 g/10 min and a bulk density of 0.42 g/cm³. There was no agglomeration of polymer particles and fouling did not take place at all in the autoclave.

Application Example 77

Random copolymerization of propylene and ethylene

Random copolymerization of propylene and ethylene was performed by carrying out the polymerization of propylene in the same manner as

1 in Application Example 1, during which 0.6 g each of ethylene was
2 introduced into the autoclave six times at intervals of 10 minutes.
3 After the completion of polymerization, unreacted monomers were
4 purged from the polymerization system. Thus there was obtained 264 g
5 of propylene-ethylene random copolymer. The copolymer was found to
6 contain 2.2% of ethylene according to infrared spectrophotometry.
7 The amount of the copolymer formed per g of the catalyst component
8 was 8700 g. The block copolymer had an MFR of 13.5 g/10 min and a
9 bulk density of 0.42g/cm³.

10 Application Example 78

11 Polymerization of 1-butene

12 Polymerization of 1-butene was performed in the same manner as
13 in Application Example 1, except that 55.0 mg of the catalyst compo-
14 nent obtained in Example 4 was used, 400 ml of isobutane was used as
15 a medium, liquefied propylene was replaced by 400 ml of 1-butene
16 (liquid), the polymerization temperature was 40°C, and the polymeri-
17 zation time was 5 hours. There was obtained 176 g of powder poly-1-
18 butene. Kc was 3200 g/g-catalyst component. The polymer had an MFR
19 of 3.8 g/10 min and a bulk density of 0.41 g/cm³. The amount of
20 ether insolubles (residues remaining after extraction with boiling
21 diethyl either for 5 hours) was 99.1%.

22 Application Example 79

23 Polymerization of 4-methyl-1-pentene

24 Polymerization of 4-methyl-1-pentene was performed in the same
25 manner as in Application Example 75, except that 77.0 mg of the cata-
26 lyst component obtained in Example 4 was used. 400 ml of 4-methyl-
27 1-pentene, was used. There was obtained 192 g of poly-4-methyl-1-
28 pentene in the powder form. Kc was 2490 g/g-catalyst component. The
29 polymer had an MFR of 3.6 g/10 min, a bulk density of 0.39 g/cm³,
30 and an ether insoluble of 98.7%.

CLAIMS:

1. A reaction product for use in a titanium containing supported catalyst component, said reaction product obtain d by contacting together,

- (a) a metal oxide or a composite of metal oxides of Group IIA, IIB, IIIA, IIIB, IVA or IVB of the Periodic Table,
- (b) a dihydrocarbyl magnesium compound represented by the formula $RMgR'$, mixtures thereof or a complex with an organic compound of aluminum, boron, beryllium or zinc, and
- (c) a hydrocarboxy group-containing compound represented by the formula $R''_q M(OR''')_n$,

wherein R and R' are the same or different and are selected from alkyl, cycloalkyl, aryl and aralkyl groups having from 1 to 20 carbon atoms, R'' is a hydrogen atom or a hydrocarbyl group selected from alkyl, alkenyl, aryl or aralkyl groups having from 1 to 20 carbon atoms, R''' is a hydrocarbyl group having from 1 to 20 carbon atoms and selected from alkyl, alkenyl, aryl, or aralkyl groups, M is selected from silicon, carbon, phosphorous, boron or aluminum, m is the valence of M and $m > q \geq 0$, $M \geq n > 0$ and $n+q$ equal m.

2. The reaction product of claim 1, wherein the contacting is performed at a temperature in the range of from -20°C to 150°C for from 0.1 to 100 hours and the molar ratio of components (a), (b) and (c) is (b)/(a)=0.01 to 10, (c)/(a)=0.01 to 10 and (c)/(b)=0.1 to 10.

3. A titanium containing supported catalyst component comprising the product obtained by contacting:

- (1) the reaction product of claim 1 or claim 2,
- (2) (d) a halogen-containing alcohol,
- (3) (e) an electron-donating compound, and
- (4) (f) a di-, tri-, or tetravalent titanium compound.

4. The titanium containing supported catalyst component of claim 3 wherein the electron-donating compound is a carboxylic acid anhydride, carboxylic acid ester, carboxylic acid halide, alcohol, or ether

5. The titanium containing supported catalyst component of claim 3 or claim 4 wherein the halogen-containing alcohol is a monohydric or polyhydric alcohol and the halogen atom is chlorine.

6. The titanium containing supported catalyst component of claim 5 wherein the halogen-containing alcohol is 2,2,2-trichloroethanol.

7. The titanium containing supported catalyst component of any of claims 3 to 6, wherein the hydrocarbyloxy group-containing compound is

$\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{Si}(n-\text{OC}_4\text{H}_9)_4$, $\text{Si}(\text{OC}_6\text{H}_5)_4$, $\text{C}_6\text{H}_5\text{Si}(\text{OC}_2\text{H}_5)_3$, $\text{C}(\text{OC}_2\text{H}_5)_4$, $\text{HC}(\text{OC}_2\text{H}_5)_3$, $\text{P}(\text{OC}_2\text{H}_5)_3$, $\text{B}(\text{OC}_2\text{H}_5)_3$, or $\text{Al}(\text{OC}_2\text{H}_5)_3$.

8. A titanium containing supported catalyst component comprising the product obtained by obtaining by contacting together

- (1) the reaction product obtained by contacting:
 - (a) SiO_2 ,
 - (b) n-butyl ethyl magnesium, and
 - (c) $\text{Si}(\text{OC}_2\text{H}_5)_4$,
- (2) (d) 2,2,2-trichloroethanol,
- (3) (e) di-n-butylphthalate, and
- (4) (f) titanium tetrachloride.

9. A catalyst system for the polymerization of olefins comprising

- (I) a titanium containing supported catalyst component as claimed in any of claims 3 to 8, and
- (II) an organometallic compound of a metal of Groups I-III of the Periodic Table.

10. The catalyst system of claim 9, wherein the organometallic compound is an organoaluminum compound represented by the formula $R''_m AlX_{3-m}$ wherein R'' is an alkyl or aryl group having from 1 to 18 carbon atoms, X is halogen and m is a number from 1 to 3.

11. A method of polymerizing one or more monoolefins having 2 to 10 carbon atoms, and optionally a diolefin having 3 to 10 carbon atoms, which polymerization is carried out in the presence of a catalyst system as claimed in claim 9 or claim 10.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int Cl 4)
A	GB-A-2 099 438 (ACC CHEMICAL CO.) * Claims * --- EP-A-0 133 383 (EXXON) * Claims * -----	1	C 08 F 4/64 C 08 F 10/00
			TECHNICAL FIELDS SEARCHED (Int Cl 4)
			C 08 F
The present search report has been drawn up for all claims			
Place of search THE HAGUE	Date of completion of the search 06-10-1986	Examiner DE ROECK R.G.	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

SEARCHED
INDEXED
SERIALIZED
FILED

THIS PAGE BLANK (USPTO)